I. General Remarks

Please consider the application in view of the following remarks.

II. Disposition of Claims

Claims 1-14, 16-27 and 29-37 and 57-61 are pending in this application. No amendments have been made herein.

III. Allowable Claims

Applicants acknowledge with appreciation that the Examiner has advised that claims 1-14, 16-27, 29-37, and 57-61 are allowable over the art of record. However, the Examiner has advised that the rejection under 35 U.S.C. § 112, 1st paragraph must be overcome.

IV. Rejection of Claims under 35 U.S.C. § 112, First Paragraph

The Examiner has maintained his rejection of claims 1-14, 16-27, 29-37, and 57-61 under 35 U.S.C. § 112, first paragraph, for reasons previously stated. Specifically, although independent claims 1, 26, 57 and 61 have been amended to limit the non-surfactant polymeric emulsifier to be "ethylacrylate/methylacrylic acid," the Examiner considers that there is "insufficient written description support in the specification for this limitation." The Examiner has stated that "there has been no evidence proffered by Applicant showing that any of these polymers [ALCOSPERSE® 747; ALCOQUEST® 747 and/or ALCOGUM ® SL-117] are indeed known as a non-surfactant 'ethylacrylate/methylacrylic acid' polymeric emulsifier as recited in the presently amended claims."

Applicants respectfully traverse this rejection and submit herewith for the Examiner's consideration the following patent application filed and published prior to Applicants' filing date: International Application No. PCT/EP2002/011268, effectively filed Nov. 6, 2001, published as WO 03/040284 A1 on May 15, 2003, and also published again later as EP 1 446

470 B1. This publication is attached hereto as Exhibit A. On page 7, at lines 18-25 of WO 03/040284 A1 (and at paragraph [0023] of EP 1 446, 470 B1), this publication states:

> Very suitable are alkali-swellable or –soluble copolymers of methacrylic acid and ethyl acrylate and optionally other comonomers, such as are exemplified in the ASE- and HASE-type Alcogum™ L and SL series polymers, marketed by National Starch & Chemical Company. Alcogum L15, which is a medium cross-linked methacrylic acid/ethylacrylate copolymer of molecular weight between 500,000 and 1000,000, is a particular example of a suitable polymer, as are Alcogum L11 and SL117.

Applicants respectfully submit that this publication thus shows that ALCOGUM ® SL117 was "indeed known as a non-surfactant 'ethylacrylate/methylacrylic acid' polymeric emulsifier" at the time Applicants filed their present application before the Examiner.

Applicants thus respectfully submit that they have met the Examiner's requirements for overcoming the rejection of the pending claims.

SUMMARY

The Examiner is requested to reconsider his rejections and to allow the application to proceed to issue.

Respectfully submitted,

Date: April 27, 2011

Karen B. Tripp, Reg. No. 30,452
Attorney at Law
P.O. Box 1301
Houston, Texas 77251-1301
(713) 658-9323 phone
(713) 658-9410 fax
ktripp@tripplaw.com e-mail

cc: Craig W. Roddy, Esq.

EXHIBT A

International Publication No. WO 03/040284 A1

European Patent Specification EP 1 446 470 B1

Based on:

International Patent Application No. PCT/EP 2002/011268

claiming priority from EP01/204217.2, filed Nov. 6, 2001

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040284 A1

(51) International Patent Classification[7]: C11D 17/00, 3/37, 3/22

(21) International Application Number: PCT/EP02/11268

(22) International Filing Date: 8 October 2002 (08.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01204217.2 6 November 2001 (06.11.2001) EP

(71) Applicant *(for AE, AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LC, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LK, LS, MN, MW, MZ, NZ, OM, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; UNILEVER HOUSE, Blackfriars, London, Greater London EC4P 4BQ (GB).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LTD** [IN/IN]; HINDUSTAN LEVER HOUSE, 165 - 166 Backbay Reclamation, 400 020 Mumbai (IN).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BEJARANO, Nancy, Iris** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR). **PRIETO, Diego** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR). **SIVEIRO, José, Daniel** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR).

(74) Agent: **DEKKER, Enno, E., J.**; Unilever NV, Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIQUID ABRASIVE CLEANING COMPOSITIONS

(57) Abstract: The invention concerns aqueous liquid abrasive cleaning compositions comprising 10-50% inorganic abrasive and a double polymeric thickening system comprising a nonionic cellulose ether and an alkali-swellable or alkali-soluble (meth)acrylate polymer.

WO 03/040284 A1

LIQUID ABRASIVE CLEANING COMPOSITIONS

Field of the invention

The invention relates to aqueous liquid compositions that comprise an abrasive and a polymeric thickening agent and that are suitable for hard surface cleaning.

Background of the invention

Liquid abrasive cleaning compositions for hard surfaces are well known in the art and used for cleaning hard surfaces generally encountered in homes and institutions, particularly in kitchens, bathrooms, toilets and the like. Such compositions typically comprise a solid abrasive, and optionally a detergent surfactant, in an aqueous medium. The solid abrasive is kept suspended in the liquid medium. This can be done, either with a combination of detergent surfactants, particularly anionic and nonionic surfactants, which together form a lamellar phase and thereby cause thickening of the liquid, or with a thickening polymer to give the liquid the required viscosity properties, or by a combination of both methods.

Even liquid abrasive cleaning compositions in which the suspending properties of the liquid are provided by the use of thickening polymers in most cases still contain a certain amount of detergent surfactant to improve the cleaning properties of the composition and provide for the desired foaming of the composition in use.

Liquid abrasive cleaning compositions that contain thickening polycarboxylates and only a minimal amount of surfactant are described in WO 01/05931.

In EP 301885 alkyl-$(EO)_n$-sulphate salts (n=1-10) are mentioned as one of the range of possible anionic surfactants in a composition comprising 25-70% inorganic abrasive. Typically used nonionic surfactants are long chain aliphatic alcohol ethoxylates and amine oxides. Typical abrasive materials include minerals such as calcite and dolomite or other materials of relatively high density and sufficient hardness.

In EP 346097 a thickening mixture is described comprising a gum-type polymer (polysaccharide) and an acrylic type polymer in a ratio and amount determined by the sigmoid curves of log (viscosity) versus log (concentration) of each polymer. The preferred polysaccharide is xanthan gum. The combination of polymers is said to give synergistic thickening properties. The thickening mixtures are disclosed to be suitable for a large variety of applications, including liquid abrasive cleaners.

A well-known problem with liquid abrasive cleaners is their tendency to leave residues of solid abrasive on the cleaned surface, which are difficult to rinse away and remain visible as a white hue. Although wide ranges of abrasives content are quoted in the patent literature, ranging from less than 1% to 80% or higher, for the normal liquid abrasive cleaner well known to the consumer the practical abrasive content is generally at least 20% and ranges up to 50%. Lower abrasive contents have been described as a way to solve the rinsing problem. Thus, compositions described in WO 97/41204 comprise 0.1-10% abrasive, up to 20% of PAS and/or LES, up to 30% of ethoxylated alcohol

nonionic surfactant, 1-30% of a co-surfactant being glycerol or mono- or polyethylene glycol or mono- or polypropylene glycol, 0.6-10% of a perfume or a water-insoluble hydrocarbon having 6-18 carbon atoms, and some other components. However, they are generally considered to compromise on cleaning ability on tough and strongly adhering soils and have so far found little use in practice.

Organic solvents have also been used in an attempt to further improve the cleaning capabilities of liquid abrasive cleaners. Thus, EP 336651 describes such compositions, containing a wide range of organic solvents with examples as diverse as 2-butoxyethanol, pine oil and limonene. The compositions all require colloidal aluminium oxide thickener to obtain a stable suspension. They preferably contain 20-40%, particularly 30% abrasive. A similar composition is described in EP 335471, comprising 1.8-4.5% of a grease-removal solvent and 10-60% of an insoluble abrasive. A wide range of anionic surfactants is mentioned for the surfactant system, the preferred ones being fatty acid soap and PAS. Another similar composition is described in EP 329209 comprising 2-10% of surfactant and 1-10% of a non- or sparingly water-soluble solvent. The surfactant is preferably a mixture of LAS and LES in a 1:1 to 4:1 ratio. The amount of abrasive is quoted to be 5-50%, but the examples all show 30%.

Japanese patent application no. 01/040600 describes cleaning compositions for cars and windows comprising surfactant, alcohol, an abrasive and a combination of a film-forming resin (preferably a polyvinyl alcohol resin) and a cellulose derivative. On top of that it may contain a thickener, which may be methylcellulose. The resin is supposed to dry out to form a film on the surface to be cleaned which traps dirt and abrasive.

The resin is present in an amount of at least 10% of the composition and the cellulose derivative in an amount of at least 0.6%, preferably at least 0.8%.

US 5,057,241 describes skin cleansing compositions comprising a thickening system consisting of hydroxypropyl cellulose or hydroxyethyl cellulose and an acrylic copolymer comprising monomeric groups possessing surfactant properties which are prepared by reacting an unsaturated acid with a nonionic surfactant. The compositions do not contain an abrasive.

US 4,830,783 discloses contact lens cleaning fluids comprising an inorganic polishing compound with an average particle size preferably below 10μm, a surfactant and a thickening agent. A large list of possible polymeric and clay thickening agents is given, among which polyacrylic acid and some cellulose derivatives, without any particular preference.

Japanese patent application no. 60/108499 describes liquid abrasive cleaning compositions comprising a surfactant, a thickener, an insoluble abrasive and a hydrocarbon solvent. The list of generally named thickeners includes polyacrylic acid, carboxycellulose and hydroxyethyl cellulose. The examples all use the clay mineral hectorite as the thickener. Similar compositions are described in DE 19918265 in which various cellulose ethers and anionic methacrylic acid/ethyl acrylate copolymers are mentioned as possible thickening agents.

In spite of the extensive prior art there is still a need to improve the rinsing properties of liquid abrasive compositions without compromising on their cleaning performance.

Furthermore, many consumers do not like the feel of liquid abrasive cleaning compositions. They are generally described as feeling grainy or rough. Therefore, there is also a need for improving the sensory properties (feel) of liquid abrasive cleaners.

Brief description of the invention

It has now been found that liquid abrasive cleaning compositions comprising between 10% and 50% inorganic abrasive in combination with a mixture of thickening polymers comprising a cellulose derivative and an alkali swellable or soluble (meth)acrylate polymer provide excellent cleaning on a large variety of soils, including tough and strongly adhering soils, are easily rinsed away and have a non-gritty and smooth feel.

Consequently, the invention also provides a process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to the invention followed by removing the soil and the composition from the surface.

Detailed description of the invention

All percentages given herein are by weight, calculated on the total composition, unless specifically indicated otherwise.

Thus, the invention provides aqueous liquid abrasive cleaning compositions comprising 10-50% inorganic abrasive and a double polymeric thickening system comprising a cellulose derivative which is a nonionic cellulose ether and an alkali-swellable or alkali-soluble (meth)acrylate polymer.

Polymeric thickening system

The cellulose derivative is a nonionic cellulose ether i.e. a cellulose derivative in which some of the cellulose hydroxy groups are replaced by methoxy or ethoxy groups and/or hydroxyethoxy or hydroxypropoxy groups. Such cellulose derivatives, which are well known in the art, are e.g. methyl-cellulose, ethyl-cellulose, hydroxyethyl-cellulose, hydroxypropyl-cellulose, hydroxyethyl-methyl- and ethyl-cellulose and hydroxypropyl-methylcellulose. Preferred are those cellulose ethers that are soluble in cold water and give increased viscosity at alkaline pH. Methyl-celluloses and their derivatives are particularly preferred, more particularly hydroxypropyl-methylcellulose. In general, those cellulose ethers are preferred which give a viscosity in 2% by weight solution in water of at least 10,000 mPa.s (Brookfield™, 20rpm, at 20°C), more preferably at least 20,000 mPa.s, most preferably between 30,000 and 55,000 mPa.s. Suitable cellulose ethers are methyl-hydroxypropyl-cellulose PMC40 US, marketed by Samsung Fine Chemicals and Culminal MHPC 45000 PFR, marketed by Hercules Inc.

The cellulose ether is used in an amount of at least 0.01%, preferably at least 0.05%. An amount of more than 1% is generally not required; preferably the amount is at most 0.5%, more preferably at most 0.3%. The amount is chosen such that the composition with cellulose ether but without the (meth)acrylate polymer has a viscosity of at most 200 mPa.s, preferably at most 100 mPa.s, more preferably at most 50mPa.s, most preferably at most 25 mPa.s (Equipment: Haake™ VT 550; measurement conditions: Rotor MV II, 21 sec^{-1} shear rate and 25°C).

The other polymer in the double polymeric thickening system is an alkali-swellable or alkali-soluble (meth)acrylate polymer. For the purposes of this invention the phrase "(meth)acrylate polymer" is defined as homo- and copolymers of acrylate and/or methacrylate monomers and optionally other vinylic monomers. Thus, it includes polyacrylate, polymethacrylate, copolymers of acrylate and methacrylate and copolymers of acrylate and/or methacrylate with other vinylic monomers such as maleic anhydride and styrene. The carboxylate groups in the polymer are preferably partly esterified. The polymer may also be cross-linked and/or hydrophobically modified. However, the polymer contains sufficient free carboxylic acid/carboxylate groups to make it alkali-swellable or alkali-soluble. The polymers have a molecular weight of at least 100,000, preferably at least 500,000.

Very suitable are alkali-swellable or -soluble copolymers of methacrylic acid and ethyl acrylate and optionally other comonomers, such as are exemplified in the ASE- and HASE-type Alcogum™ L and SL series polymers, marketed by National Starch & Chemical Company. Alcogum L15, which is a medium cross-linked methacrylic acid/ethyl acrylate copolymer of molecular weight between 500,000 and 1000,000, is a particular example of a suitable polymer, as are Alcogum L11 and SL117.

(Meth)acrylate polymers suitable for the invention have in 1% (by weight of dry solids) solution in water at 20°C and pH 8 a viscosity of at least 500 mPa.s and at most 50,000 mPa.s (Broookfield™, 10rpm), preferably at least 1000 and at most 30,000.

The (meth)acrylate polymer is generally used in an amount of at least 0.1%, preferably at least 0.2%, more preferably at least 0.4%. Amounts of more than 4% are not normally required to obtain sufficient viscosity. Generally the amount is at most 2%, preferably at most 1%.

The two components of the double polymeric thickening system are generally used in a (meth)acrylate polymer/cellulose ether ratio of between 20:1 and 1:1, preferably between 10:1 and 2:1, more preferably between 7:1 and 2:1.

The liquid abrasive cleaning compositions according to the invention have such fluid flow characteristics that they are stable suspensions when not in use, but thin enough to be poured from the packaging container and spread on the soiled surface without appearing thin and watery. Thus, the components and amounts of the thickening system are chosen in such a way that the composition has a viscosity between 300 and 5000 mPa.s, preferably 300-3000 mPa.s, more preferably 500-2500, most preferably 900-1800 mPa.s. (Equipment: Haake™ VT 550; measurement conditions: Rotor MV II, 21 sec^{-1} shear rate and 25°C).

Abrasive

An inorganic abrasive is an essential component of the composition. The amount of abrasive in the cleaning compositions according to the invention is preferably at least 15%, more preferably at least 20%, but preferably does not exceed 45% or even 40%. Preferred abrasives have a Moh hardness of below 6, but above 1, preferably at least 2, although abrasives with

higher hardness than 6 can be employed for specialist applications.

Suitable inorganic abrasives can be selected from water-soluble and water-insoluble materials. Soluble abrasives are present in an amount exceeding their solubility in water and the 10-50% amount of abrasive material then refers to the amount present as insoluble material. Examples of such materials are to be found among alkali metal carbonates, phosphates, sulphates, borates and chlorides, such as Na bicarbonate, Na borate, Na tripolyphosphate, K sulphate, water-free Ca sulphate. Suitable water-insoluble abrasives are zeolites, silica's, silicates, carbonates and aluminas. Water-insoluble abrasives are preferred and preferred examples are: Ca carbonate (e.g. as calcite), mixtures of Ca and Mg carbonates (e.g. as dolomite), alumina, hydrated alumina, feldspar, talc and silica. Calcite and dolomite are particularly preferred due to their low cost and good abrasive properties.

Preferred weight average particle sizes for the abrasives fall in the range 1-500 microns, with values of 5-100 microns being particularly preferred.

The compositions according to the invention preferably have pH between 5 and 14, more preferably at least 7. An alkaline pH improves the cleaning properties, particularly on fatty soils and pH values between 8 and 13 are very suitable. For alkali metal and alkaline earth metal carbonates and bicarbonate abrasives an alkaline pH is required.

Optional surfactants

To further improve the cleaning properties and preferably provide a certain degree of foaming of the product when in use, the compositions according to the invention preferably contain one or more detergent surfactants. They may be chosen from a wide range of anionic, nonionic, zwitterionic and amphoteric surfactants well known in the art. For liquid abrasive cleaning compositions anionic and/or nonionic surfactants are most often chosen as the principle surfactant and for the purposes of the present invention nonionic surfactants are particularly preferred.

Synthetic anionic surfactants may be chosen from the alkali metal, alkaline earth metal, ammonium or alkanolammonium salts of the well known organic sulphuric acid esters and sulphonic acids having in the molecular structure a branched or straight chain alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

Examples of such anionic surfactants are water-soluble salts of:

- long chain (i.e. 6-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced from tallow or coconut oil or the synthetic alcohols derived from petroleum;
- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;

- sulphates of ethoxylated aliphatic alcohols containing 1-10 ethyleneoxy units per molecule;
- alkylphenol ethyleneoxy-ether sulphates containing 1-10 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralized with alkali.

A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain that is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB. Particular examples include:

- the condensation products of aliphatic alcohols having from 6 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol ethylene oxide condensates having from 1 to 15 moles of ethylene oxide per mole of coconut alcohol;
- condensates of alkylphenols having C6-C15 alkyl groups with 2 to 25 moles of ethylene oxide per mole of alkylphenol;
- condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 2,000 to 15,000.

Other classes of nonionic surfactants are:

- alkylpolyglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
- tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 6 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 6 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 8 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

Amphoteric or zwitterionic surfactants may be used as additional surfactants. Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 6 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate. Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.

Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949; Vol.2 by Schwartz, Perry & Berch, Interscience 1958; in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn. Carl Hauser Verlag, 1981.

The total amount of surfactant is usually 0 - 4%, preferably, 0.1 - 2%, more preferably 0.2 - 1%. Preferably the total surfactant in the composition according to the invention consists primarily or entirely of nonionic surfactant. Ethoxylated aliphatic alcohols are particularly preferred nonionic surfactants.

An organic solvent may optionally be present in the compositions according to the invention. Various hydrocarbons (e.g. mineral oil derived or terpenoid), alcohols, polyols and polyol ethers have been described as suitable solvents for use in liquid abrasive cleaning compositions. Preferred are mono- and di-ethylene glycol mono-ethers and mono- and di-propylene glycol mono-ethers. Mono- and di-propylene glycol mono-(C_1-C_5)alkyl ethers are particularly suitable. When present the amount is kept below 5%, preferably below 2%, more preferably below 1%, but preferably at least 0.1%.

The compositions according to the invention may further comprise well-known optional components to further enhance their properties in use, such as builders, antifoams, preservatives, antimicrobials, etc. They may also comprise components to enhance their consumer appeal such as colorants, pigments and

perfume. They may contain bleaching agents provided that the other components in the composition are stable in their presence

As outlined above, the invention also provides a process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to the invention, followed by removing the soil and the composition from the surface. The composition may be appplied to the surface straight from the container and the surface thereafter cleaned by loosening the soil from the surface with a wet wipe, cloth, sponge or similar implement rubbing the composition over the surface. Alternatively the composition is first applied to a wipe, cloth or sponge which may be prewetted with water, wherafter the soil is loosened from the surface by rubbing the implement with the composition over the surface. The treatment is completed by removing the soil and the composition from the surface, either with an implement or by rinsing the surface with water.

Examples:

Stable liquid abrasive cleaning compositions having excellent cleaning properties on a variety of soils were prepared having the compositions given in the table below:

	Example 1	Example 2
C_9-C_{11} Ethoxylated fatty alcohol 6OE	0.600	0.600
Sodium hydroxide	0.125	0.106
Alcogum L15	0.70	0.55
Calcium Carbonate (Omyacarb A30)	30.00	30.0
PMC 40US *	0.140	0.220
1.2 benzothiazolin-3-one	0.016	0.016
Dipropylene glycol n-butyl ether	0.60	-
Water	To 100%	

* Hydroxypropyl-methyl-cellulose supplied by Samsung Fine Chemicals.

The PCM 40US was premixed with sufficient water to obtain a thick, but pourable liquid mix. To the remainder of the water Alcogum, sodium hydroxide, abrasive, surfactant, the PCM 40US premix and the solvent (Example 1) were added, preferably in that order. Thereafter preservative and/or perfume was added, if desired. The final mixture of Example 1 had a viscosity of 1250 mPa.s at 21 sec^{-1} (Haake VT550, rotor MVII). The same composition, but without added PCM 40US, has a viscosity of 500 mPa.s, whereas the same mixture with PCM 40US but without Alcogum has a viscosity of less than 50 mPa.s.

The sensory properties of the product according to example 1 were compared with those of a commercial product containing 20% calcite, 4.7% anionic/2.1% nonionic self-structuring surfactant mixture, 1% butyl digol solvent and 0.03% Acusol 820 polycarboxylate. A panel of 20 consumers judged both products on creaminess and consistency using a scale of 1-5. The average rating on creaminess of example 1 was 3.8 versus 2.0 for the commercial product; the average rating on consistency for example 1 was 3.7, versus 2.3 for the commercial product. The product according to example 1 was often commented on as having a silky feel

Both products were also compared as to the ease with which the abrasive is removed after cleaning, using the test method described below by 20 panellists:
5 g product are poured on a dark blue decamel table. The product is removed using a wet double Ballerina™ cloth (20x10cm), making 1 rinsing cycle of 10 circular wipes of 20-30cm diameter, whereafter it is observed whether foam or abrasive residues are still visible on the decamel surface. If necessary more rinsing cycles are performed until all residues had disappeared, using a freshly washed and rinsed wet Ballerina cloth each time.
The test result is expressed as the number of wiping cycles needed to completely remove the product.
On average the product of Example 1 required 1.2 wiping cycles, whereas the market product required 4.3 wiping cycles.

CLAIMS

1. Aqueous liquid abrasive cleaning compositions comprising an inorganic abrasive and a polymeric thickener characterised in that it comprises:
   - 10-50% of inorganic abrasive;
   - a double polymeric thickening system comprising a nonionic cellulose ether in an amount of 0.01-1% and an alkali-swellable or alkali-soluble (meth)acrylate polymer having a molecular weight of at least 100,000 in an amount of 0.1-4%

2. Cleaning composition according to claim 1 characterised in that the amount of cellulose derivative is 0.05-0.5%.

3. Cleaning composition according to claims 1-2 characterised in that the cellulose ether is a methylcellulose or derivative thereof.

4. Cleaning composition according to claim 3 characterised in that the cellulose ether is methyl-hydroxypropylcellulose.

5. Cleaning composition according to claims 1-4 characterised in that cellulose ethers are chosen which give a viscosity in 2% solution in water of at least 10,000 mPa.s.

6. Cleaning composition according to claims 1-5 characterised in that the amount of alkali-swellable or alkali-soluble (meth)acrylate polymer is 0.2-2%.

7. Cleaning composition according to claims 1-6 characterised in that a (meth)acrylate polymer is chosen which has in 1% solution in water at 20°C and pH 8 a viscosity of between 500 and 50,000 mPa.s.

8. Cleaning composition according to claim 6 or 7 characterised in that the (meth)acrylate polymer is a copolymer of methacrylic acid and ethyl acrylate and optionally other comonomers.

9. Cleaning composition according to claims 1-8 characterised in that the two components of the double polymeric thickening system are used in a (meth)acrylate polymer/cellulose ether ratio of between 20:1 and 1:1.

10. Cleaning composition according to claims 1-9 characterised in that the abrasive is chosen from calcium carbonate, mixtures of calcium and magnesium carbonates, zeolite, alumina, hydrated alumina, feldspar, talc and silica and has a particle size of 5-100 micron.

11. Cleaning composition according to claims 1-10 characterised in that it contains a surfactant in an amount of up to 4%.

12. Cleaning composition according to claim 11 characterised in that it contains a nonionic surfactant in an amount of 0.1-4%.

13. A process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to any one of claims 1-12 and removing the soil and the composition from the surface.

INTERNATIONAL SEARCH REPORT

In onal Application No
PCT/EP 02/11268

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D17/00 C11D3/37 C11D3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 057 241 A (MERRITT COLLEEN M ET AL) 15 October 1991 (1991-10-15) cited in the application column 19 -column 20; claims; examples ---	1-13
A	US 4 830 783 A (SALAMONE JOSEPH C ET AL) 16 May 1989 (1989-05-16) cited in the application column 3 -column 4; claims; example 7 column 18 --- -/--	1-13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 December 2002	10/01/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Pfannenstein, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int onal Application No
PCT/EP 02/11268

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198530 Derwent Publications Ltd., London, GB; Class A97, AN 1985-180798 XP002194662 & JP 60 108499 A (LION CORP), 13 June 1985 (1985-06-13) cited in the application abstract	1-13
A	DE 199 18 265 A (HENKEL KGAA) 26 October 2000 (2000-10-26) cited in the application page 4; claims; examples 1,3	1-13

INTERNATIONAL SEARCH REPORT

Int ›nal Application No
PCT/EP 02/11268

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5057241	A	15-10-1991	AU	4109589 A	24-05-1990
			JP	2180809 A	13-07-1990
US 4830783	A	16-05-1989	US	4394179 A	19-07-1983
			AU	537744 B2	12-07-1984
			AU	5931080 A	08-01-1981
			CA	1152843 A1	30-08-1983
			DE	3021034 A1	08-01-1981
			FR	2459993 A1	16-01-1981
			GB	2055118 A ,B	25-02-1981
			IT	1131637 B	25-06-1986
			JP	1724390 C	24-12-1992
			JP	3081136 B	27-12-1991
			JP	56006215 A	22-01-1981
			US	4534878 A	13-08-1985
JP 60108499	A	13-06-1985	JP	1781618 C	13-08-1993
			JP	4072880 B	19-11-1992
DE 19918265	A	26-10-2000	DE	19918265 A1	26-10-2000
			AU	5210100 A	10-11-2000
			CA	2306397 A1	22-10-2000
			WO	0065019 A1	02-11-2000

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 446 470 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
08.02.2006 Bulletin 2006/06

(21) Application number: **02777294.6**

(22) Date of filing: **08.10.2002**

(51) Int Cl.:
C11D 17/00 *(2006.01)* ***C11D 3/37*** *(2006.01)*
C11D 3/22 *(2006.01)*

(86) International application number:
PCT/EP2002/011268

(87) International publication number:
WO 2003/040284 (15.05.2003 Gazette 2003/20)

(54) **LIQUID ABRASIVE CLEANING COMPOSITIONS**

FLÜSSIGE SCHEUERMITTEL

COMPOSITIONS DETERGENTES ABRASIVES LIQUIDES

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

(30) Priority: **06.11.2001 EP 01204217**

(43) Date of publication of application:
18.08.2004 Bulletin 2004/34

(73) Proprietors:
- **UNILEVER N.V.**
  3013 AL Rotterdam (NL)
  Designated Contracting States:
  AT BE BG CH CZ DE DK EE ES FI FR GR IT LU MC NL PT SE SK TR
- **UNILEVER PLC**
  London, Greater London EC4P 4BQ (GB)
  Designated Contracting States:
  CY GB IE

(72) Inventors:
- **BEJARANO, Nancy, Iris,**
  Unilever de Argentina SA
  1427 Buenos Aires (AR)
- **PRIETO, Diego,**
  Unilever de Argentina SA
  1427 Buenos Aires (AR)
- **SIVEIRO, José, Daniel,**
  Unilever de Argentina SA
  1427 Buenos Aires (AR)

(74) Representative: **Dekker, Enno Ernst Jan et al**
Unilever Patent Group
Olivier van Noortlaan 120
3133 AT Vlaardingen (NL)

(56) References cited:
DE-A- 19 918 265 **US-A- 4 830 783**
US-A- 5 057 241

- **DATABASE WPI Section Ch, Week 198530 Derwent Publications Ltd., London, GB; Class A97, AN 1985-180798 XP002194662 & JP 60 108499 A (LION CORP), 13 June 1985 (1985-06-13) cited in the application**

EP 1 446 470 B1

Description

Field of the invention

[0001] The invention relates to aqueous liquid compositions that comprise an abrasive and a polymeric thickening agent and that are suitable for hard surface cleaning.

Background of the invention

[0002] Liquid abrasive cleaning compositions for hard surfaces are well known in the art and used for cleaning hard surfaces generally encountered in homes and institutions, particularly in kitchens, bathrooms, toilets and the like. Such compositions typically comprise a solid abrasive, and optionally a detergent surfactant, in an aqueous medium. The solid abrasive is kept suspended in the liquid medium. This can be done, either with a combination of detergent surfactants, particularly anionic and nonionic surfactants, which together form a lamellar phase and thereby cause thickening of the liquid, or with a thickening polymer to give the liquid the required viscosity properties, or by a combination of both methods.

[0003] Even liquid abrasive cleaning compositions in which the suspending properties of the liquid are provided by the use of thickening polymers in most cases still contain a certain amount of detergent surfactant to improve the cleaning properties of the composition and provide for the desired foaming of the composition in use.

[0004] Liquid abrasive cleaning compositions that contain thickening polycarboxylates and only a minimal amount of surfactant are described in WO 01/05931.

[0005] In EP 301885 alkyl-$(EO)_n$-sulphate salts (n=1-10) are mentioned as one of the range of possible anionic surfactants in a composition comprising 25-70% inorganic abrasive. Typically used nonionic surfactants are long chain aliphatic alcohol ethoxylates and amine oxides. Typical abrasive materials include minerals such as calcite and dolomite or other materials of relatively high density and sufficient hardness.

[0006] In EP 346097 a thickening mixture is described comprising a gum-type polymer (polysaccharide) and an acrylic type polymer in a ratio and amount determined by the sigmoid curves of log (viscosity) versus log (concentration) of each polymer. The preferred polysaccharide is xanthan gum. The combination of polymers is said to give synergistic thickening properties. The thickening mixtures are disclosed to be suitable for a large variety of applications, including liquid abrasive cleaners.

[0007] A well-known problem with liquid abrasive cleaners is their tendency to leave residues of solid abrasive on the cleaned surface, which are difficult to rinse away and remain visible as a white hue. Although wide ranges of abrasives content are quoted in the patent literature, ranging from less than 1% to 80% or higher, for the normal liquid abrasive cleaner well known to the consumer the practical abrasive content is generally at least 20% and ranges up to 50%. Lower abrasive contents have been described as a way to solve the rinsing problem. Thus, compositions described in WO 97/41204 comprise 0.1-10% abrasive, up to 20% of PAS and/or LES, up to 30% of ethoxylated alcohol nonionic surfactant, 1-30% of a co-surfactant being glycerol or mono- or polyethylene glycol or mono- or polypropylene glycol, 0.6-10% of a perfume or a water-insoluble hydrocarbon having 6-18 carbon atoms, and some other components. However, they are generally considered to compromise on cleaning ability on tough and strongly adhering soils and have so far found little use in practice.

[0008] Organic solvents have also been used in an attempt to further improve the cleaning capabilities of liquid abrasive cleaners. Thus, EP 336651 describes such compositions, containing a wide range of organic solvents with examples as diverse as 2-butoxyethanol, pine oil and limonene. The compositions all require colloidal aluminium oxide thickener to obtain a stable suspension. They preferably contain 20-40%, particularly 30% abrasive. A similar composition is described in EP 335471, comprising 1.8-4.5% of a grease-removal solvent and 10-60% of an insoluble abrasive. A wide range of anionic surfactants is mentioned for the surfactant system, the preferred ones being fatty acid soap and PAS. Another similar composition is described in EP 329209 comprising 2-10% of surfactant and 1-10% of a non- or sparingly water-soluble solvent. The surfactant is preferably a mixture of LAS and LES in a 1:1 to 4:1 ratio. The amount of abrasive is quoted to be 5-50%, but the examples all show 30%.

[0009] Japanese patent application no. 01/040600 describes cleaning compositions for cars and windows comprising surfactant, alcohol, an abrasive and a combination of a film-forming resin (preferably a polyvinyl alcohol resin) and a cellulose derivative. On top of that it may contain a thickener, which may be methylcellulose. The resin is supposed to dry out to form a film on the surface to be cleaned which traps dirt and abrasive.

[0010] The resin is present in an amount of at least 10% of the composition and the cellulose derivative in an amount of at least 0.6%, preferably at least 0.8%.

[0011] US 5,057,241 describes skin cleansing compositions comprising a thickening system consisting of hydroxypropyl cellulose or hydroxyethyl cellulose and an acrylic copolymer comprising monomeric groups possessing surfactant properties which are prepared by reacting an unsaturated acid with a nonionic surfactant. The compositions do not contain an abrasive.

[0012] US 4,830,783 discloses contact lens cleaning fluids comprising an inorganic polishing compound with an average particle size preferably below 10μm, a surfactant and a thickening agent. A large list of possible polymeric and clay thickening agents is given, among which polyacrylic acid and some cellulose derivatives, without any particular preference.

[0013] Japanese patent application no. 60/108499 describes liquid abrasive cleaning compositions comprising a surfactant, a thickener, an insoluble abrasive and a hydrocarbon solvent. The list of generally named thickeners includes polyacrylic acid, carboxycellulose and hydroxyethyl cellulose. The examples all use the clay mineral hectorite as the thickener. Similar compositions are described in DE 19918265 in which various cellulose ethers and anionic methacrylic acid/ethyl acrylate copolymers are mentioned as possible thickening agents.

[0014] In spite of the extensive prior art there is still a need to improve the rinsing properties of liquid abrasive compositions without compromising on their cleaning performance.

[0015] Furthermore, many consumers do not like the feel of liquid abrasive cleaning compositions. They are generally described as feeling grainy or rough. Therefore, there is also a need for improving the sensory properties (feel) of liquid abrasive cleaners.

Brief description of the invention

[0016] It has now been found that liquid abrasive cleaning compositions comprising between 10% and 50% inorganic abrasive in combination with a mixture of thickening polymers, in amounts as defined in claim 1, comprising a nonionic cellulose ether and an alkali swellable or soluble (meth)acrylate polymer which has molecular weight of at least 100,000, provide excellent cleaning on a large variety of soils, including tough and strongly adhering soils, are easily rinsed away and have a non-gritty and smooth feel.

[0017] Consequently, the invention also provides a process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to the invention followed by removing the soil and the composition from the surface.

Detailed description of the invention

[0018] All percentages given herein are by weight, calculated on the total composition, unless specifically indicated otherwise.

[0019] Thus, the invention provides an aqueous liquid abrasive cleaning composition according to claim 1.

Polymeric thickening system

[0020] The nonionic cellulose ether is a cellulose derivative in which some of the cellulose hydroxy groups are replaced by methoxy or ethoxy groups and/or hydroxyethoxy or hydroxypropoxy groups. Such cellulose derivatives, which are well known in the art, are e.g. methyl-cellulose, ethyl-cellulose, hydroxyethyl-cellulose, hydroxypropyl-cellulose, hydroxyethyl-methyl- and ethyl-cellulose and hydroxypropyl-methylcellulose. Preferred are those cellulose ethers that are soluble in cold water and give increased viscosity at alkaline pH. Methyl-celluloses and their derivatives are particularly preferred, more particularly hydroxypropyl-methylcellulose. In general, those cellulose ethers are preferred which give a viscosity in 2% by weight solution in water of at least 10,000 mPa.s (Brookfield™, 20rpm, at 20°C), more preferably at least 20,000 mPa.s, most preferably between 30,000 and 55,000 mPa.s. Suitable cellulose ethers are methyl-hydroxypropyl-cellulose PMC40 US, marketed by Samsung Fine Chemicals and Culminal MHPC 45000 PFR, marketed by Hercules Inc.

[0021] The cellulose ether is used in an amount of at least 0.01%, preferably at least 0.05%. An amount of more than 1% is not required; preferably the amount is at most 0.5%, more preferably at most 0.3%. The amount is chosen such that the composition with cellulose ether but without the (meth)acrylate polymer has a viscosity of at most 200 mPa.s, preferably at most 100 mPa.s, more preferably at most 50mPa.s, most preferably at most 25 mPa.s (Equipment: Haake™ VT 550; measurement conditions: Rotor MV II, 21 sec^{-1} shear rate and 25°C).

[0022] The other polymer in the double polymeric thickening system is an alkali-swellable or alkali-soluble (meth)acrylate polymer. For the purposes of this invention the phrase "(meth)acrylate polymer" is defined as homo- and copolymers of acrylate and/or methacrylate monomers and optionally other vinylic monomers. Thus, it includes polyacrylate, polymethacrylate, copolymers of acrylate and methacrylate and copolymers of acrylate and/or methacrylate with other vinylic monomers such as maleic anhydride and styrene. The carboxylate groups in the polymer are preferably partly esterified. The polymer may also be cross-linked and/or hydrophobically modified. However, the polymer contains sufficient free carboxylic acid/carboxylate groups to make it alkali-swellable or alkali-soluble. The polymers have a molecular weight of at least 100,000, preferably at least 500,000.

[0023] Very suitable are alkali-swellable or -soluble copolymers of methacrylic acid and ethyl acrylate and optionally other comonomers, such as are exemplified in the ASE- and HASE-type Alcogum™ L and SL series polymers, marketed

by National Starch & Chemical Company. Alcogum L15, which is a medium cross-linked methacrylic acid/ethyl acrylate copolymer of molecular weight between 500,000 and 1000,000, is a particular example of a suitable polymer, as are Alcogum L11 and SL117.

[0024] (Meth)acrylate polymers suitable for the invention have in 1% (by weight of dry solids) solution in water at 20°C and pH 8 a viscosity of at least 500 mPa.s and at most 50,000 mPa.s (Broookfield™, 10rpm), preferably at least 1000 and at most 30,000.

[0025] The (meth)acrylate polymer is used in an amount of at least 0.1%, preferably at least 0.2%, more preferably at least 0.4%. Amounts of more than 4% are not required to obtain sufficient viscosity. Generally the amount is at most 2%, preferably at most 1%.

[0026] The two components of the double polymeric thickening system are generally used in a (meth)acrylate polymer/cellulose ether ratio of between 20:1 and 1:1, preferably between 10:1 and 2:1, more preferably between 7:1 and 2:1.

[0027] The liquid abrasive cleaning compositions according to the invention have such fluid flow characteristics that they are stable suspensions when not in use, but thin enough to be poured from the packaging container and spread on the soiled surface without appearing thin and watery. Thus, the components and amounts of the thickening system are chosen in such a way that the composition has a viscosity between 300 and 5000 mPa.s, preferably 300-3000 mPa.s, more preferably 500-2500, most preferably 900-1800 mPa.s. (Equipment: Haake™ VT 550; measurement conditions: Rotor MV II, 21 sec^{-1} shear rate and 25°C).

Abrasive

[0028] An inorganic abrasive is an essential component of the composition. The amount of abrasive in the cleaning compositions according to the invention is preferably at least 15%, more preferably at least 20%, but preferably does not exceed 45% or even 40%. Preferred abrasives have a Moh hardness of below 6, but above 1, preferably at least 2, although abrasives with higher hardness than 6 can be employed for specialist applications.

[0029] Suitable inorganic abrasives can be selected from water-soluble and water-insoluble materials. Soluble abrasives are present in an amount exceeding their solubility in water and the 10-50% amount of abrasive material then refers to the amount present as insoluble material. Examples of such materials are to be found among alkali metal carbonates, phosphates, sulphates, borates and chlorides, such as Na bicarbonate, Na borate, Na tripolyphosphate, K sulphate, water-free Ca sulphate.

Suitable water-insoluble abrasives are zeolites, silica's, silicates, carbonates and aluminas. Water-insoluble abrasives are preferred and preferred examples are: Ca carbonate (e.g. as calcite), mixtures of Ca and Mg carbonates (e.g. as dolomite), alumina, hydrated alumina, feldspar, talc and silica. Calcite and dolomite are particularly preferred due to their low cost and good abrasive properties.

[0030] Preferred weight average particle sizes for the abrasives fall in the range 1-500 microns, with values of 5-100 microns being particularly preferred.

[0031] The compositions according to the invention preferably have pH between 5 and 14, more preferably at least 7. An alkaline pH improves the cleaning properties, particularly on fatty soils and pH values between 8 and 13 are very suitable. For alkali metal and alkaline earth metal carbonates and bicarbonate abrasives an alkaline pH is required.

Optional surfactants

[0032] To further improve the cleaning properties and preferably provide a certain degree of foaming of the product when in use, the compositions according to the invention preferably contain one or more detergent surfactants. They may be chosen from a wide range of anionic, nonionic, zwitterionic and amphoteric surfactants well known in the art. For liquid abrasive cleaning compositions anionic and/or nonionic surfactants are most often chosen as the principle surfactant and for the purposes of the present invention nonionic surfactants are particularly preferred.

[0033] Synthetic anionic surfactants may be chosen from the alkali metal, alkaline earth metal, ammonium or alkanolammonium salts of the well known organic sulphuric acid esters and sulphonic acids having in the molecular structure a branched or straight chain alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

[0034] Examples of such anionic surfactants are water-soluble salts of:

- long chain (i.e. 6-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced from tallow or coconut oil or the synthetic alcohols derived from petroleum;
- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-10 ethyleneoxy units per molecule;
- alkylphenol ethyleneoxy-ether sulphates containing 1-10 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralized with alkali.

[0035] A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain that is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB. Particular examples include:

- the condensation products of aliphatic alcohols having from 6 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol ethylene oxide condensates having from 1 to 15 moles of ethylene oxide per mole of coconut alcohol;
- condensates of alkylphenols having C6-C15 alkyl groups with 2 to 25 moles of ethylene oxide per mole of alkylphenol;
- condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 2,000 to 15,000.

[0036] Other classes of nonionic surfactants are:

- alkylpolyglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
- tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 6 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 6 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 8 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

[0037] Amphoteric or zwitterionic surfactants may be used as additional surfactants. Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 6 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate. Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.

[0038] Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949; Vol.2 by Schwartz, Perry & Berch, Interscience 1958; in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn. Carl Hauser Verlag, 1981.

[0039] The total amount of surfactant is usually 0 - 4%, preferably, 0.1 - 2%, more preferably 0.2 - 1%. Preferably the total surfactant in the composition according to the invention consists primarily or entirely of nonionic surfactant. Ethoxylated aliphatic alcohols are particularly preferred nonionic surfactants.

[0040] An organic solvent may optionally be present in the compositions according to the invention. Various hydrocarbons (e.g. mineral oil derived or terpenoid), alcohols, polyols and polyol ethers have been described as suitable solvents for use in liquid abrasive cleaning compositions. Preferred are mono- and diethylene glycol mono-ethers and mono- and di-propylene glycol mono-ethers. Mono- and di-propylene glycol mono-(C_1-C_5)alkyl ethers are particularly suitable. When present the amount is kept below 5%, preferably below 2%, more preferably below 1%, but preferably at least 0.1%.

[0041] The compositions according to the invention may further comprise well-known optional components to further enhance their properties in use, such as builders, antifoams, preservatives, antimicrobials, etc. They may also comprise components to enhance their consumer appeal such as colorants, pigments and perfume. They may contain bleaching agents provided that the other components in the composition are stable in their presence

[0042] As outlined above, the invention also provides a process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to the invention, followed by removing the soil and the composition from the surface. The composition may be appplied to the surface straight from the container and the surface thereafter cleaned by loosening the soil from the surface with a wet wipe, cloth, sponge or similar implement rubbing the composition over the surface. Alternatively the composition is first applied to a wipe, cloth or sponge which may be prewetted with water, wherafter the soil is loosened from the surface by rubbing the implement with the composition over the surface. The treatment is completed by removing the soil and the composition from the surface, either with an implement or by rinsing the surface with water.

Examples:

[0043] Stable liquid abrasive cleaning compositions having excellent cleaning properties on a variety of soils were prepared having the compositions given in the table below:

	Example 1	Example 2
C_9-C_{11} Ethoxylated fatty alcohol 6OE	0.600	0.600
Sodium hydroxide	0.125	0.106
Alcogum L15	0.70	0.55
Calcium Carbonate (Omyacarb A30)	30.00	30.0
PMC 40US *	0.140	0.220
1.2 benzothiazolin-3-one	0.016	0.016
Dipropylene glycol n-butyl ether	0.60	-
Water	To 100%	
* Hydroxypropyl-methyl-cellulose supplied by Samsung Fine Chemicals.		

[0044] The PCM 40US was premixed with sufficient water to obtain a thick, but pourable liquid mix. To the remainder of the water Alcogum, sodium hydroxide, abrasive, surfactant, the PCM 40US premix and the solvent (Example 1) were added, preferably in that order. Thereafter preservative and/or perfume was added, if desired. The final mixture of Example 1 had a viscosity of 1250 mPa.s at 21 sec^{-1} (Haake VT550, rotor MVII). The same composition, but without added PCM 40US, has a viscosity of 500 mPa.s, whereas the same mixture with PCM 40US but without Alcogum has a viscosity of less than 50 mPa.s.

[0045] The sensory properties of the product according to example 1 were compared with those of a commercial product containing 20% calcite, 4.7% anionic/2.1% nonionic self-structuring surfactant mixture, 1% butyl digol solvent and 0.03% Acusol 820 polycarboxylate. A panel of 20 consumers judged both products on creaminess and consistency using a scale of 1-5. The average rating on creaminess of example 1 was 3.8 versus 2.0 for the commercial product; the average rating on consistency for example 1 was 3.7, versus 2.3 for the commercial product. The product according to example 1 was often commented on as having a silky feel

[0046] Both products were also compared as to the ease with which the abrasive is removed after cleaning, using the test method described below by 20 panellists:

> 5 g product are poured on a dark blue decamel table. The product is removed using a wet double Ballerina™ cloth (20x10cm), making 1 rinsing cycle of 10 circular wipes of 20-30cm diameter, whereafter it is observed whether foam or abrasive residues are still visible on the decamel surface. If necessary more rinsing cycles are performed until all residues had disappeared, using a freshly washed and rinsed wet Ballerina cloth each time.

The test result is expressed as the number of wiping cycles needed to completely remove the product.
On average the product of Example 1 required 1.2 wiping cycles, whereas the market product required 4.3 wiping cycles.

Claims

1. Aqueous liquid abrasive cleaning compositions comprising an inorganic abrasive and a polymeric thickener **char-**

acterised in that it comprises:

- 10-50% of inorganic abrasive;
- a double polymeric thickening system comprising a nonionic cellulose ether in an amount of 0.01-1% and an alkali-swellable or alkali-soluble (meth)acrylate polymer having a molecular weight of at least 100,000 in an amount of 0.1-4%

and wherein the composition has a viscosity between 300 and 5000 mPa.s.

2. Cleaning composition according to claim 1 **characterised in that** the amount of cellulose derivative is 0.05-0.5%.

3. Cleaning composition according to claims 1-2 **characterised in that** the cellulose ether is a methylcellulose or derivative thereof.

4. Cleaning composition according to claim 3 **characterised in that** the cellulose ether is methyl-hydroxypropylcellulose.

5. Cleaning composition according to claims 1-4 **characterised in that** cellulose ethers are chosen which give a viscosity in 2% solution in water of at least 10,000 mPa.s.

6. Cleaning composition according to claims 1-5 **characterised in that** the amount of alkali-swellable or alkali-soluble (meth)acrylate polymer is 0.2-2%.

7. Cleaning composition according to claims 1-6 **characterised in that** a (meth)acrylate polymer is chosen which has in 1% solution in water at 20°C and pH 8 a viscosity of between 500 and 50,000 mPa.s.

8. Cleaning composition according to claim 6 or 7 **characterised in that** the (meth)acrylate polymer is a copolymer of methacrylic acid and ethyl acrylate and optionally other comonomers.

9. Cleaning composition according to claims 1-8 **characterised in that** the two components of the double polymeric thickening system are used in a (meth)acrylate polymer/cellulose ether ratio of between 20:1 and 1:1.

10. Cleaning composition according to claims 1-9 **characterised in that** the abrasive is chosen from calcium carbonate, mixtures of calcium and magnesium carbonates, zeolite, alumina, hydrated alumina, feldspar, talc and silica and has a particle size of 5-100 micron.

11. Cleaning composition according to claims 1-10 **characterised in that** it contains a surfactant in an amount of up to 4%.

12. Cleaning composition according to claim 11 **characterised in that** it contains a nonionic surfactant in an amount of 0.1-4%.

13. A process for cleaning hard surfaces comprising the steps of applying to the surface a composition according to any one of claims 1-12 and removing the soil and the composition from the surface.

Patentansprüche

1. Wässerige flüssige Scheuerreinigungszusammensetzungen, umfassend ein anorganisches Scheuermittel und ein polymeres Verdickungmittel, **dadurch gekennzeichnet, dass** es

- 10 - 50 % anorganisches Scheuermittel,
- ein doppeltes polymeres Verdickungssystem, umfassend einen nicht-ionischen Celluloseether in einer Menge von 0,01 - 1 % und ein Alkali-quellfähiges oder Alkali-lösliches (Meth)Acrylatpolymer mit einem Molekulargewicht von mindestens 100.000 in einer Menge von 0,1 - 4 %, umfasst,

und wobei die Zusammensetzung eine Viskosität zwischen 300 und 5.000 mPa.s aufweist.

2. Reinigungszusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** die Menge des Cellulosederivats 0,05 - 0,5 % beträgt.

3. Reinigungszusammensetzung nach den Ansprüchen 1 bis 2, **dadurch gekennzeichnet, dass** der Celluloseether eine Methyl-cellulose oder ein Derivat davon ist.

4. Reinigungszusammensetzung nach Anspruch 3, **dadurch gekennzeichnet, dass** der Celluloseether Methyl-hydroxypropylcellulose ist.

5. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die Celluloseether derart ausgewählt sind, dass sie in einer 2%igen Lösung in Wasser eine Viskosität von mindestens 10.000 mPa.s ergeben.

6. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die Menge des Alkaliquellfähigen oder Alkali-löslichen (Meth)Acrylatpolymers 0,2 bis 2 % beträgt.

7. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** ein (Meth)Acrylatpolymer gewählt wird, das in einer 1%igen Lösung in Wasser bei 20° C und pH 8 eine Viskosität zwischen 500 und 50.000 mPa.s aufweist.

8. Reinigungszusammensetzung nach Anspruch 6 oder 7, **dadurch gekennzeichnet, dass** das (Meth)Acrylatpolymer ein Copolymer von Methacrylsäure und Ethylacrylat und ggf. anderen Comonomeren ist.

9. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** die zwei Komponenten des doppelten polymeren Verdickungssystems in einem Verhältnis von (Meth)Acrylatpolymer/Celluloseether zwischen 20:1 und 1:1 verwendet werden.

10. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** das Scheuermittel aus Calciumcarbonat, Gemischen von Calcium- und Magnesiumcarbonaten, Zeolith, Aluminiumoxid, hydratisiertem Aluminiumoxid, Feldspat, Talkum und Siliziumdioxid ausgewählt ist und eine Partikelgröße von 5 bis 100 µm aufweist.

11. Reinigungszusammensetzung nach einem der Ansprüche 1 bis 10, **dadurch gekennzeichnet, dass** sie ein oberflächenaktives Mittel in einer Menge von bis zu 4·% enthält.

12. Reinigungszusammensetzung nach Anspruch 11, **dadurch gekennzeichnet, dass** sie ein nicht-ionisches oberflächenaktives Mittel in einer Menge von 0,1 bis 4 % enthält.

13. Verfahren zur Reinigung harter Oberflächen, umfassend die Schritte Auftragen einer Zusammensetzung nach einem der Ansprüche 1 bis 12 auf die Oberfläche und Entfernen des Schmutzes und der Zusammensetzung von der Oberfläche.

Revendications

1. Composition aqueuse détergente abrasive liquide comprenant un abrasif inorganique et un épaississant polymérique **caractérisé en ce qu'**elle comprend :

   - 10 à 50 % d'abrasif inorganique;
   - un double système épaississant polymérique comprenant un éther de cellulose non ionique en quantité de 0,01 à 1 % et un polymère (méth)-acrylate capable de gonfler ou soluble en milieu alcalin ayant une masse moléculaire au moins égale à 100 000 en une quantité de 0,1 à 4 %,

   et dans laquelle la composition a une viscosité entre 300 et 5000 mPa.s.

2. Composition détergente selon la revendication 1 **caractérisée en ce que** la quantité de dérivé cellulosique est de 0,05 à 0,5 %.

3. Composition détergente selon les revendications 1 à 2 **caractérisée en ce que** l'éther de cellulose est une méthylcellulose ou un dérivé de celle-ci.

4. Composition détergente selon la revendication 3 **caractérisée en ce que** l'éther de cellulose est une méthylhydroxypropylcellulose.

5. Composition détergente selon les revendications 1 à 4 **caractérisée en ce que** les éthers de celluloses choisis donnent une viscosité en solution à 2 % dans l'eau au moins égale à 10 000 mPa.s.

6. Composition détergente selon les revendications 1 à 5 **caractérisée en ce que** la quantité de polymère (méth)acrylate capable de gonfler ou soluble en milieu alcalin est de 0,2 à 2 %.

7. Composition détergente selon les revendications 1 à 6 **caractérisée en ce qu'**un polymère (méth)-acrylate choisi possède, en solution à 1 % dans l'eau à 20°C et pH 8, une viscosité entre 500 et 50 000 mPas.

8. Composition détergente selon la revendication 6 ou 7 **caractérisée en ce que** le polymère (méth)-acrylate est un copolymère d'acide méthacrylique et d'acrylate d'éthyle et de manière facultative d'autres comonomères.

9. Composition détergente selon les revendications 1 à 8 **caractérisée en ce que** les deux composants du double système épaississant polymérique sont utilisés dans un rapport polymère (méth)acrylate/éther de cellulose entre 20/1 et 1/1.

10. Composition détergente selon les revendications 1 à 9 **caractérisée en ce que** l'abrasif est choisi dans le groupe comprenant le carbonate de calcium, les mélanges de carbonates de calcium et de magnésium, la zéolite, l'alumine, l'hydrate d'alumine, le feldspath, le talc et la silice et possède une taille de particule de 5 à 100 μm.

11. Composition détergente selon les revendications 1 à 10 **caractérisée en ce qu'**elle contient un surfactant en quantité jusqu'à 4 %.

12. Composition détergente selon la revendication 11 **caractérisée en ce qu'**elle contient un surfactant non ionique en quantité de 0,1 à 4 %.

13. Procédé de nettoyage de surfaces dures comprenant les étapes consistant à appliquer sur la surface une composition selon l'une quelconque des revendications 1 à 12 et à éliminer de la surface la salissure et la composition.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040284 A1

(51) International Patent Classification[7]: C11D 17/00, 3/37, 3/22

(21) International Application Number: PCT/EP02/11268

(22) International Filing Date: 8 October 2002 (08.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01204217.2 6 November 2001 (06.11.2001) EP

(71) Applicant *(for AE, AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LC, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LK, LS, MN, MW, MZ, NZ, OM, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; UNILEVER HOUSE, Blackfriars, London, Greater London EC4P 4BQ (GB).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LTD** [IN/IN]; HINDUSTAN LEVER HOUSE, 165 - 166 Backbay Reclamation, 400 020 Mumbai (IN).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BEJARANO, Nancy, Iris** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR). **PRIETO, Diego** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR). **SIVEIRO, José, Daniel** [AR/AR]; Unilever de Argentina SA, Fraga 1163, 1427 Buenos Aires (AR).

(74) Agent: **DEKKER, Enno, E., J.**; Unilever NV, Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/040284 A1

(54) Title: LIQUID ABRASIVE CLEANING COMPOSITIONS

(57) Abstract: The invention concerns aqueous liquid abrasive cleaning compositions comprising 10-50% inorganic abrasive and a double polymeric thickening system comprising a nonionic cellulose ether and an alkali-swellable or alkali-soluble (meth)arcylate polymer.